

PATENT SPECIFICATION.



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PROVISIONAL SPECIFICATION.

Improvements relating to the Manufacture of Acetic Acid, Acetaldehyde or Acetone or Mixtures Containing the same.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of 8, Waterloo Place, London, S.W. 1, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of acetic acid, acetaldehyde, or acetone or mixtures containing the same.

According to the invention a mixture containing methane and carbon dioxide or carbon monoxide or both oxides, is passed over a heated catalytic material capable of effecting combination between the methane and the oxide or oxides of carbon to form the acetic acid, acetaldehyde, acetone or mixture of any of these.

In particular I may employ catalytic material consisting of or comprising nickel carbonate or other carbonates of metals which usually dissociate at temperatures between about 100° and about 500° C. with formation of oxide and evolution of carbon dioxide. It is found that such carbonates effect or assist the reaction catalytically, perhaps owing to their assuming a labile phase or undergoing rapidly alternating decarbonation and carbonation when heated in the presence of the mixture of methane and carbon dioxide or carbon monoxide or both. The metals of which they are carbonates may or may not be themselves metals which are catalysts for the reaction.

The carbonate may be mixed or associated with metallic nickel or other metal or metals which are catalysts for or tend to promote the reaction, for example cobalt, copper, iron, palladium, platinum, palladium black or platinum black.

It is understood that mixtures of such carbonates as referred to may be em-

ployed, with or without a free catalytic or reaction-promoting metal or metals. Other carbonates, such as sodium carbonate, may likewise be employed in association with the carbonate or carbonates such as before referred to, with or without free catalytic or reaction-promoting metal or metals.

In carrying out the invention the carbon dioxide or monoxide or mixture of carbon dioxide and monoxide will usually be employed in a large excess relatively to the methane and the reaction will be conducted at a temperature above the distilling point of the aliphatic compound or compounds formed.

The catalytic material may be employed in any suitable or convenient form, whether deposited on porous materials, or as wire, gauze or in other finely divided state or otherwise.

The operation may be carried out in tubes, pipes, chambers or any other suitable form of apparatus. Usually it will be conducted under high pressure which may for example be between five and 100 atmospheres or more, but I do not confine myself in this respect.

The operation may be conducted as a continuous process by recirculating the reaction gases through the conversion chamber or chambers, and separating the desired aliphatic conversion product or products after successive passages or at other desired intervals.

The invention may be illustrated by the following example of one form in which it may be carried out for the production of acetic acid or mixtures containing the same, it being understood that this is given only by way of example and can be varied widely.

A mixture of methane with a very

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large excess of carbon dioxide is passed under pressure (e.g. about 12 to 50 atmospheres) through pipes or chambers filled with or containing nickel carbonate, preferably mixed with finely divided nickel, at a temperature above the boiling point of acetic acid, e.g. between about 120° and 200° C. The mixture of gas and vapour resulting is led on to apparatus for separating the acetic acid or mixture of acetic acid and other aliphatic compounds formed, and the residual methane and carbon dioxide

are recirculated through the conversion chambers, as a continuous process, further additions of methane and carbon dioxide being made at intervals as required. 15

Dated this 21st day of June, 1923.

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COMPLETE SPECIFICATION.

Improvements relating to the Manufacture of Acetic Acid, Acetaldehyde or Acetone or Mixtures Containing the same.

I, HENRY DREYFUS, of 8, Waterloo Place, London, S.W. 1, a citizen of the Swiss Republic, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of acetic acid, acetaldehyde, or acetone or mixtures containing the same. 35

According to the invention a mixture containing methane and carbon dioxide or carbon monoxide or both oxides, is passed under pressure and at temperatures below about 500° C. in contact with a catalyst or catalysts of either or both of the following classes: Catalysts of the so-called hydrogenation class, such as copper, iron, nickel, cobalt, palladium, platinum, palladium black or platinum black; nickel carbonate or other metal carbonates which usually dissociate at temperatures between about 100° and about 500° C., with formation of oxide and evolution of carbon dioxide. It is found that such carbonates effect or assist the reaction catalytically, perhaps owing to their assuming a labile phase or undergoing rapidly alternating decarbonation and carbonation when heated in the presence of the mixture of methane and carbon dioxide or carbon monoxide or both. 50

The carbonate may be mixed or associated with the metallic nickel or others of the catalytic metals before referred to. 60

It is understood that mixtures of such carbonates as referred to may be employed, with or without a free catalytic or reaction-promoting metal or metals. Other carbonates, such as sodium carbonate, may likewise be employed in association with the carbonate or carbonates such as before referred to, with

or without free catalytic or reaction-promoting metal or metals. 70

It has been proposed to produce formaldehyde and methyl alcohol by causing reaction between methane and carbon dioxide at high temperatures (e.g. 500° to 700° C.) without pressure, in presence of catalysts, in which reaction oxidation of the methane is thought to be effected by oxygen liberated by decomposition of the carbon dioxide at the high temperature. 80

By effecting reaction between methane and carbon dioxide or/and carbon monoxide under pressure at lower temperatures in presence of catalysts such as hereinbefore referred to, I have found that this leads to the formation of acetaldehyde, acetic acid or acetone or mixtures containing the same. 85

In carrying out the invention the carbon dioxide or monoxide or mixture of carbon dioxide and monoxide will usually be employed in excess relatively to the methane. The reaction may be carried out in tubes, pipes, chambers, or any other suitable form of apparatus. 90

The catalytic material may be employed in any suitable or convenient form, whether deposited on porous materials, or as wire, gauze or in other finely divided state or otherwise. Or the catalytic or reaction-promoting metal or material may itself form partly or entirely the tubes, chambers or apparatus in which the reaction takes place, with or without employment of catalytic or reaction-promoting material in the interior thereof. For instance, iron tubes or reaction chambers may themselves serve as the catalytic or reaction-promoting material. 100 105 110

The reaction is conducted under pressure. For instance one may employ pres-

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tures between five and 100 atmospheres or more.

The rate of passage of the mixed gases over the catalytic or reaction-promoting material depends upon the temperature and pressure. The higher the temperature and the higher the pressure, the quicker the speed of passage of the gases.

The operation may be conducted as a continuous process by recirculating the reaction gases through the conversion chamber or chambers, and separating the desired aliphatic conversion product or products after successive passages or at other desired intervals.

The invention may be illustrated by the following examples, it being understood that these are given only by way of example and can be varied widely.

A mixture of methane with an excess of carbon monoxide over the molecular proportion theoretically required for the production of acetaldehyde, *e.g.* an excess of about 10 to 20% of CO, is passed under a pressure of about 12 to 50 atmospheres, at a temperature of about 150°–300° C. through pipes or chambers filled with or containing the catalytic or reaction-promoting material, *e.g.* finely divided iron, or nickel carbonate, the latter preferably mixed with finely divided nickel. The speed of passage of the gases varies with the temperature and pressure. At 12 to 50 atmospheres and 150°–300° C. it may, for example, be about 1 to 20 litres per minute. The mixture of gas and vapour resulting is led to apparatus for separating the acetaldehyde or mixture of aldehyde and other aliphatic compounds formed, and the residual methane and carbon monoxide are recirculated through the conversion chambers, as a continuous process, further additions of methane and carbon monoxide being made at intervals as required.

As another example a mixture of methane with an excess of carbon dioxide over the molecular proportion theoretically required for the production of acetic acid, *e.g.* an excess of about 20%, is passed under pressure, *e.g.* about 12 to 50 atmospheres, through pipes or chambers filled with or containing the catalytic or reaction-promoting material, *e.g.* finely divided iron, or nickel carbonate, the latter preferably mixed with finely

divided nickel or iron, at a temperature above the boiling point of acetic acid, *e.g.* between about 120° and 300° C. The speed of passage of the gases varies with the temperature and pressure. At 10 to 50 atmospheres and temperatures between 120° and 300° it may be for example between about 1 and 20 litres per minute. The mixture of gas and vapour resulting is led on to apparatus for separating the acetic acid or mixture of acetic acid and other aliphatic compounds formed, and the residual methane and carbon dioxide are recirculated through the conversion chambers as a continuous process, further additions of methane and carbon dioxide being made at intervals as required.

Mixtures of both carbon monoxide and carbon dioxide with methane may be similarly employed.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. Process for the production of acetic acid, acetaldehyde or acetone or mixtures containing the same, characterised in that a mixture containing methane and carbon monoxide or carbon dioxide or both oxides, is passed under pressure and at temperature below about 500° C. in contact with a catalyst or catalysts of either or both of the classes referred to, *viz.* catalysts of the so called hydrogenation class, such as iron, nickel, cobalt, palladium, platinum, palladium black, platinum black or copper; or nickel carbonate or other metal carbonates which usually dissociate between about 100° and 500° C., with formation of oxide and liberation of carbon dioxide.

2. In a process according to Claim 1, the employment in association with nickel carbonate or other metal carbonate of the character referred to, of other carbonates, such as sodium carbonate.

3. Process for the production of acetaldehyde, acetic acid or acetone or mixtures containing the same, substantially as hereinbefore described.

Dated this 17th day of April, 1924.

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